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(54) Process for the preparation of an olefins-containing mixture of hydrocarbons.

(57) Process for the preparation of an olefins-containing mixture of hydrocarbons, which process comprises contacting a hydrocarbonaceous feedstock with a zeolitic catalyst at a temperature above 480 °C during less than 10 seconds, whereby the catalyst/feedstock weight ratio is in the range from 5 to 150 and the zeolitic catalyst comprises a zeolite with a pore diameter of 0.3 to 0.7 nm and an average crystalline size of less than 2 micrometer.

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The present invention relates to a process for the preparation of an olefins-containing mixture of hydrocarbons.

There is considerable interest in the production of olefins, especially ethylene and propylene, as their reactivity renders them suitable for conversion to further products, in contrast to the low value lower paraffins.

It is known to convert hydrocarbonaceous feedstocks, such as light distillates, to products rich in lower olefins, especially ethylene and propylene, by high temperature steam cracking. The typical product slate obtained in such steam cracking processes is not entirely suited to the needs of the chemical industry in that it represents a relatively high methane production level and a high ratio of ethylene to propylene.

There have recently been developed alternative processes for the production of lower olefins, for example as described in EP 0347003, EP 0392590 and EP 0385538, from a wide range of hydrocarbonaceous feedstocks. Those processes have been found to give surprisingly high yiels of lower olefins, low amounts of methane and a low ratio of ethylene to propylene and C_4 olefins when compared with conventional steam cracking.

Ethylene and propylene are valuable starting materials for chemical processes, while C_4 olefins can find use as a starting material for alkylation and/or oligomerization procedures in order to produce high octane gasoline and/or middle distillates. Isobutene can be usefully converted to methyl t-butyl ether.

Surprisingly, it has now been found that even higher yields of lower olefins and lower ratios of ethylene to propylene can be obtained in comparison with the above-cited processes if use is made of a zeolitic catalyst comprising a zeolite having a specific average crystallite size.

Accordingly, the present invention relates to process for the preparation of an olefins-containing mixture of hydrocarbons, which process comprises contacting a hydrocarbonaceous feedstock with a zeolitic catalyst at a temperature above 480 °C during less than 10 seconds, whereby the catalyst/feedstock weight ratio is in the range from 5 to 150 and the zeolitic catalyst comprises a zeolite with a pore diameter of 0.3 to 0.7 nm and an average crystallite size of less than 2 micrometer.

Preferably, the zeolitic catalyst to be applied in the process according to the present invention comprises a zeolite having an average crystallite size of less than 1 micrometer. More preferably, the zeolite has an average crystallite size in the range of 0.01 to 0.5 micrometer.

The term crystallite size in this specification is to be regarded as the size of the individual zeolite crystals. These individual crystals may agglomerate into clusters which each may comprise 3 to 10 or more individual crystals. Preferably the zeolite comprises separate individual crystals.

The zeolitic catalyst to be used may comprise one or more zeolites with a pore diameter of from 0.3 to 0.7 nm, preferably from 0.5 to 0.7 nm.

The term zeolite in this specification is not to be regarded as comprising only crystalline aluminosilicates. The term also includes crystalline silica (silicalite), silicoaluminophosphates (SAPO), chromosilicates, gallium silicates, iron silicates, aluminium phosphates (ALPO), titanium aluminosilicates (TASO), boron silicates, titanium aluminophosphates (TAPO) and iron aluminosilicates.

Suitable examples include crystalline silica (silicalite), silicoaluminophosphates (SAPO), chromosilicates, gallium silicates, iron silicates, aluminium phosphates (ALPO), titanium aluminosilicates (TASO), boron silicates, titanium aluminophosphates (TAPO) and iron aluminosilicates. Examples of the zeolite include SAPO-4 and SAPO-11, which are described in US-A-4,440,871, ALPO-11, described in US-A-4,310,440, TAPO-11, desribed in US-A-4,500,651, TASO-45 described in US-A-4,254,297, aluminium silicates like erionite, ferrierite, theta and the ZSM-type zeolites such as ZSM-5, ZSM-11, ZSM-12, ZSM-35, ZSM-23, and ZSM-38. Preferably the zeolite with a pore diameter of from 0.3 to 0.7 nm is selected from the group consisting of crystalline (metallo)silicates having a ZSM-5 structure, ferrierite, erionite and mixtures thereof. Preferably, the zeolite with a pore diameter of from 0.3 to 0.7 nm comprises a crystalline (metallo)silicate having a ZSM-5 structure. Suitable examples of crystalline (metallo)silicates with ZSM-5 structure are aluminium, gallium, iron, scandium, rhodium and/or chromium silicates as described in e.g. GB-B-2,110,559.n

After the preparation of the zeolites to be used in the present process usually a significant amount of alkali metal oxide is present in the readily prepared zeolites. Preferably, the amount of alkali metal is removed by methods known in the art, such as ion-exchange, optionally followed by calcination, to yield the zeolite in its hydrogen form.

Preferably, the zeolite used in the process according to the present invention is substantially in its hydrogen form.

The catalyst suitably further comprises a matrix comprising a refractory oxide that serves as binder material. Suitable refractory oxides include alumina, silica, silica-alumina, magnesia, titania, zirconia and mixtures thereof. The matrix may further comprise natural or synthetic clays. The weight ratio of refractory

oxide and zeolite suitably ranges from 10:90 to 99:1, preferably from 50:50 to 90:10. The zeolitic catalyst may comprise up to about 40% by weight of further zeolites with a pore diameter above 0.7 nm. Suitable examples of such zeolites include the faujasite-type zeolites, zeolite beta, zeolite omega and in particular zeolite X and Y. The zeolitic catalyst comprises a zeolite with a pore diameter of from 0.3 to 0.7 nm. Suitably the zeolitic catalyst comprises ZSM-5 and zeolite Y.

The hydrocarbonaceous feedstock is contacted with the zeolitic catalyst for less than 10 seconds. Suitably, the minimum contact time is 0.1 second. Very good results are obtained when the hydrocarbonaceous feedstock is contacted with the zeolitic catalyst during 0.2 to 6 seconds.

The process is carried out at a relatively high temperature. A preferred temparature range is 480 to 900 °C, more preferably 500 to 750 °C.

The pressure to be used in the process according to the present invention can be varied within wide ranges. It is, however, preferred that the pressure is such that at prevailing temperature the mixture of hydrocarbons obtained is substantially in its gaseous phase or brought thereto by contact with the catalyst. This can be advantageous since no expensive compressors and high-pressure vessels and other equipment are necessary. A suitable pressure range is from 1 to 10 bar. Subatmospheric pressures are possible, but not preferred. It can be economically advantageous to operate at atmospheric pressure. Other gaseous materials may be present during the conversion of the hydrocarbonaceous feedstock such as steam and/or nitrogen.

Olefin production is facilitated by the absence of hydrogen or a hydrogen donor. Hence, the present invention is advantageously carried out in the absence of added hydrogen. It is, of course, possible that during the reaction some small molecules, such as hydrogen molecules are formed. However, this amount is usually negligible and will be less than than 0.5 %wt of the product.

The process according to the present invention may be carried out in a fixed bed. However, this would imply that extremely high space velocities be required to attain the short contact times envisaged. Therefore, the present invention is preferably carried out in a moving bed. The bed of catalyst may move upwards or downwards. When the bed moves upwards a process somewhat similar to a fluidized catalytic cracking process is obtained.

In the process according to the present invention some coke forms on the catalyst. Therefore it is advantageous to regenerate the catalyst. Preferably, the catalyst is regenerated by subjecting it to a treatment with an oxidizing gas, such as air. An continuous regeneration, similar to the regeneration carried out in a fluidized catalytic cracking process, is especially preferred.

The coke formation does not occur at a very high rate. Hence, it would be possible to arrange for a process in which the residence time of the catalyst particles in a reaction zone, e.g. a moving bed, is longer than the residence time of the feedstock in the reaction zone. Of course the contact time between feedstock and catalyst should be less than 10 seconds. The contact time generally corresponds with the residence time of the feedstock. Suitably the residence time of the catalyst is from 1 to 20 times the residence time of the feedstock.

The weight ratio of the catalyst used relative to the hydrocarbonaceous feedstock to be converted (catalyst/oil ratio, g/g) may vary widely,viz. from 5 up to 150 kg catalyst per kg of the hydrocarbonaceous feedstock. Preferably, the weight ratio of catalyst relative to the hydrocarbonaceous feedstock is from 10 to 100, more preferably from 20 to 100. Apart from the substantial gain in lower olefins production it has been found that at (relatively) high catalyst/feedstock weight ratios far less coke is produced with small crystallite zeolites than with large crystallite zeolites.

It is especially the combination of high temperature, short contact time, use of the specific small crystallite catalyst and (relatively) high catalyst/feedstock weight ratio which allows an attractive high conversion to olefins and low coke make.

The hydrocarbonaceous feedstock which is to be contacted with the zeolitic catalyst in the process of the present invention can vary within a wide boiling range. Examples of suitable feedstocks are relatively light petroleum fractions such as feedstocks comprising C_{3-4} hydrocarbons (e.g. LPG), naphtha, gasoline fractions and kerosine fractions. Heavier feedstocks may comprise, for example, vacuum distillates, long residues, deasphalted residual oils and atmospheric distillates, for example gas oils and vacuum gas oils. Another attractive feedstock comprises a mixture of hydrocarbons obtained in a Fischer-Tropsch hydrocarbon synthesis process.

The invention will now be illustrated by way of the following

EXAMPLE

Experiment 1.

The hydrocarbonaceous feedstock in this experiment was a hydrowax having the following properties:

IBP, °C	298
20 %wt	388
50 %wt	433
90 %wt	495
FBP	552
density 70/4	0.8057 kg/l
nitrogen	1.0 ppmw

The feedstock was contacted in a downflow reactor by passing it downwards co-currently with a flow of catalyst particles. The catalyst comprised ZSM-5 in a silica-alumina matrix (weight ratio ZSM-5/silica-alumina 25:75). The ZSM-5 had an average crystallite size of 0.1 micrometer. The experiment was carried out at a pressure of 2 bar. Further process conditions and the results obtained are given in Table 1 as shown hereinbelow.

Experiment 2 was carried out for the purpose of comparison in substantially the similar manner as experiment 1, except that now a ZSM-5 was used having a conventional crystallite size ranging from 3 to 7 micrometer. The results obtained are given in Table 1 as shown herein below.

TABLE 1

Experiment No.	1	2
Process conditions:		
Reactor temperature, °C	580	580
Catalyst/oil ratio, g/g	87	87
contact time, s	1.2	1.7
Product, %wt on feed		
C_1	2.7	2.4
C_2	1.4	1.5
$C_2^=$	11.9	13.3
C_3	1.4	2.6
$C_3^=$	36.3	32.3
C_4	0.6	0.8
$C_4^=$	22.8	16.2
C_5-220 °C	7.1	9.3
221-425 °C	9.8	5.6
425 °C+	0.7	8.2
Coke	4.6	7.8

Experiments 3 and 4 were carried out in substantially the same manner as Experiments 1 and 2 respectively. The results obtained are given in Table 2 as shown herein below.

TABLE 2

Experiment No.	3	4
Process conditions:		
Reactor temperature, °C	587	583
Catalyst/oil ratio, g/g	29	24
contact time, s	1.05	1.65
Product, %wt on feed		
hydrogen	0.7	0.6
C_1	3.4	2.8
C_2	1.8	2.8
$C_2^=$	10.2	10.3
C_3	0.8	6.5
$C_3^=$	27.7	18.8
C_4	0.0	3.8
$C_4^=$	18.1	11.0
C_5-220 °C	17.2	19.3
221-425 °C	15.5	17.6
425 °C+	2.3	4.5
Coke	2.3	2.0

From the above it will be clear that the results obtained in the experiments according to the present invention are more attractive in terms of lower olefins yields and coke make than those obtained in the comparative experiment.

Claims

1. Process for the preparation of an olefins-containing mixture of hydrocarbons, which process comprises contacting a hydrocarbonaceous feedstock with a zeolitic catalyst at a temperature above 480 °C during less than 10 seconds, whereby the catalyst/feedstock weight ratio is in the range from 5 to 150 and the zeolitic catalyst comprises a zeolite with a pore diameter of 0.3 to 0.7 nm and an average crystallite size of less than 2 micrometer.

2. Process according to claim 1, wherein the zeolite has an average crystallite size of less than 1 micrometer.

3. Process according to claim 2, wherein the zeolite has an average crystallite size in the range of 0.01 to 0.5 micrometer.

4. Process according to any one of claims 1-3, wherein the zeolite has a pore diameter of 0.5 to 0.7 nm.

5. Process according to any one of claims 1-4, wherein the zeolite is selected from crystalline (metallo)-silicates having a ZSM-5 structure, ferrierite, erionite and mixtures thereof.

6. Process according to any one of claims 1-5, wherein the zeolite is substantially in its hydrogen form.

7. Process according to any one of claims 1-6, wherein the feedstock is contacted with the zeolitic catalyst during 0.2 to 6 seconds.

8. Process according to any one of claims 1-7, wherein the temperature is from 480 to 900 °C.

9. Process according to claim 8, wherein the temperature is from 500 to 750 °C.

10. Process according to any one of claims 1-9, wherein the pressure is from 1 to 10 bar.

11. Process according to any one of claims 1-10, wherein the catalyst/feedstock weight ratio is from 10 to 100.

12. Process according to any one of claims 1-11, which is carried out in a moving bed of catalyst.

13. A hydrocarbonaceous product, or a fraction thereof, when obtained by the process of any one of claims 1-12.

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EUROPEAN SEARCH REPORT

Application Number

EP 91 20 3184

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
D,Y D,A	EP-A-0 385 538 (SHELL) * claims 1,2,3,4,5,6,7,8,10 * * page 3, line 9 * * example 1 * ---	1,5,6,8 4,7,9, 10,11	C10G11/05
Y A	FR-A-2 217 408 (MOBIL) * claims 1,7 * * page 6, line 17 - page 6, line 19 * * examples 21,22 * -----	1,5,6,8 2,3,7, 12,13	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C10G

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	03 MARCH 1992	DE HERDT O.C.E.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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